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14. ABSTRACT Oxides catalyze many reactions that convert alkanes or carbon dioxide to high-value chemicals, but very few achieve the conversion and the selectivity necessary for commercial application. The principal investigator (PI) used quantum mechanics to search for surface modifications that will improve catalytic performance of oxides. He examined three kinds of modifications. (1) The substitution of some of the cations of the oxide with other cations (e.g. replace some Ce atoms in CeO ₂ with La). (2) The deposition of a submonolayer of oxide clusters of one kind on an oxide of a different kind (e.g. VO _x clusters on the surface of CeO ₂). (3) Halogenate the oxide surface by adsorbing halogens or by substituting some oxygen atoms with halogens. Given the limited knowledge of surface structure and composition of working catalysts and the approximation inherent in the calculations, the PI emphasized the search for qualitative trends and design principles which guided experiments performed in collaboration with colleagues. The main conclusion of these studies is that all these modifications improve catalytic performance of oxides.					
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Final Technical Report, AFOSR FA9550-09-1-0333, “Catalysis by Atomic-Sized Centers: Methane Activation for Partial Oxidation and Combustion”

Industrial organic chemistry, which uses oil to produce plastics, rubber, dyes, detergents, fuels, drugs, cosmetics, fabrics, etc., needs a new cheap and reliable source of carbon. It is the opinion of many prominent chemists that natural gas is our best alternative for the next hundred years. The use of methane -- as an oil replacement -- encounters several difficulties. (1) The existing technology for methane conversion to the products now obtained from oil is too expensive. (2) Much of the existing methane is in small fields, in remote locations with harsh climates. Transporting this “stranded methane” to the place of use is too costly. We need new technology to convert it, on site, to useful liquids that are easy to transport over large distances. (3) Finally, in some deposits the natural gas contains large amounts of “impurities” such as CO₂ or sulfur-containing compounds, whose presence increases the cost of conversion.

To convert our oil-based chemical industry into one based on natural gas, we need better catalysts for alkane processing. In this project, the PI has focused on methane, which is the main ingredient of natural gas. The same principles are now applied by him to the other components of natural gas, ethane, propane and butane.

Many experiments have shown that oxides catalyze most of the reactions needed for replacing oil with natural gas. Unfortunately, they do not achieve the conversion and the selectivity necessary for commercial application. The goal of the PI is to use theoretical chemistry and experiments to find how to modify oxide surfaces to make them better catalysts. This grant funded the theoretical aspects of this research program.

The PI examined three kinds of surface modifications. 1. The substitution of some of the cations of the oxide with other cations (e.g. replace some Ce atoms in CeO₂ with La) or in other words, substitutional doping of the cations. 2. The deposition of a submonolayer of oxide clusters of one kind on an oxide of a different kind (e.g. VO_x clusters on the surface of CeO₂). 3. The “halogenation” of the oxide surface, that is, the adsorption of a small amount of halogen on the surface of the oxide while the oxide is used to catalyze alkane activation.

The PI is keenly aware of the fact that we do not know in detail the morphology and the composition of a working oxide catalyst, which consists of a material with very high surface area in contact with gases at high pressure (one atmosphere or higher). Because of this his work

emphasizes the discovery of qualitative trends and design principles rather than detailed analysis of each step in the reaction mechanism. The main practical goal is to find rules that will reduce the number of experiments made while searching for better catalysts. His scientific goal is to find guiding principles and rules that will allow a more systematic organization of our knowledge of catalysis. Finally, he is collaborating with experimentalists to verify some of the predictions and test the recommendations based on calculations.

The applications are to partial oxidation of alkanes and to the use of CO₂ as a milder alkane oxidant than oxygen.

A. Catalysis by doped oxides. This part of the work is based on the assumption that substitutional doping of an oxide can improve its catalytic performance. An example of such doping is LaCeO₂, a material in which a fraction of the Ce atoms in CeO₂ are replaced with La. This is not a mixture of La₂O₃ and CeO₂ but a homogeneous (one-phase) material having the fluorite structure of CeO₂. The premise of the work is that by choosing the proper combination of dopant and host oxide, the doped oxide will be a better catalyst than the host oxide. In the above example it is assumed that LaCeO₂ has substantially different catalytic activity than either CeO₂ or La₂O₃. The question that the work of the PI aims to answer is whether we can find dopant-host oxide combinations that are substantially better catalysts than either oxide.

The premise of the work is that the presence of the dopant in the surface of the oxide disrupts the bonding in the system. This disruption may make the oxygen atoms near the dopant more reactive or may activate the dopant. The work of the PI has documented that both effects take place, depending on which dopant is combined with which oxide. He also found rules that predict for a given oxide which dopants will improve catalytic activity. The main difficulty in the implementation of these rules is the synthesis of the appropriate doped oxides.

The goals of this part of the project are

1. Find the best oxide-dopant pair for catalytic activation of alkanes or of CO₂.
2. Find general, qualitative rules to guide doped-oxide catalyst design.
3. Understand the connection between the catalytic chemistry of doped oxides and their electronic structure.

Numerous calculations, on a variety of oxides, led the PI to classify dopants into three classes, which are defined below.

A1. Low-valence dopants (LVDs). By definition a low-valence dopant is one whose valence is lower than that of the cation it replaces in the host oxide. For example, a La dopant in CeO_2 is a low-valence dopant because La is trivalent when it combines with oxygen (it makes La_2O_3) and Ce is tetravalent. We do not need to do any calculation to know that La is an LVD when it dopes ceria. However, consider a Nb dopant in ceria. Nb has three stable oxides NbO , NbO_2 and Nb_2O_5 and is not *a priori* clear whether Nb dopant in CeO_2 is a low-valence dopant or not. We need to perform quantum mechanical calculations to determine whether Nb in this example is a LVD. There are many examples in which one can state without calculations whether a dopant in a given oxide is an LVD. For such cases the PI has shown that all such dopant have a number of very similar properties which can be counted on without performing further calculations.

A2. High-valence dopants (HVDs)in irreducible oxides. These are dopants whose valence, in all their *stable* oxides, is higher than that of the cation they substitute in the host oxide. For example, Ce has two oxides, Ce_2O_3 and CeO_2 , which are substantially more stable than all other Ce oxides. Therefore, the valence of a Ce dopant can be either III or IV. A cerium dopant in an *irreducible* oxide such as CaO is a HVD. The PI has found common rules of behavior for all HVD in irreducible oxide and this is why he classifies them as a class.

A3. High-valence dopants (HVDs) in reducible oxides. Consider the example of W dopant in CeO_2 , which is a reducible oxide, and in ZrO_2 , which is irreducible. The chemical effects of doping ZrO_2 with W are very different than those that W has on CeO_2 . The reason is that Ce^{4+} ions in CeO_2 are easily reduced to Ce^{3+} . When W dopes CeO_2 , two electrons from W are used to reduce Ce^{4+} ions to Ce^{3+} . Thus high-valence dopants in irreducible oxides lose their high valence: the W dopant in the above example has only 4 electrons for making bonds with the oxide, not 6. These events change the chemistry of such doped oxides and the PI found that they need to be classified separately. Doping ZrO_2 with W has a very different effect on surface chemistry than doping CeO_2 with W.

A4. Flexible-valence oxides (FVDS). These are dopants that have *several stable oxides*. For example, Mo makes two very stable oxides, MoO_2 and MoO_3 , so we assign it two possible valences, IV and VI. If Mo is used to dope Ta_2O_5 it can take a valence of IV, in which case it will act as an LVD, or a valence of VI, in which case it will act as an HVD. We call Mo a

flexible-valence dopant because we do not know *a priori* what valence it will take when used as a dopant and therefore it is difficult to guess the behavior of the doped oxide.

This nomenclature refers to an oxide-dopant pair. For example, La, which has one stable oxide, La_2O_3 , is an LVD if it dopes CeO_2 but a HVD if it dopes CaO .

This classification is based on numerous calculations, performed by the PI's group or by other groups. They allow researchers to guess some of the catalytic properties of a given dopant-oxide pair prior to performing any calculations. Sections B and C lay out the properties of these classes of dopant and explain why the PI grouped them the way he did.

B. The common properties of low-valence dopants

B1. LVDs make it easier to make oxygen vacancies. In what follows the term '*surface oxygen*' designates the oxygen atoms that are part of the outermost oxygen layer in the oxide and '*adsorbed oxygen*' designates oxygen atoms or molecules adsorbed from the gas phase. The ease of making an oxygen vacancy is commonly used as an indicator of the ability of the surface to function as an oxidant: the easier it is to make a vacancy, the better an oxidant the surface is. Earlier work of the PI¹⁴⁻¹⁸ has shown that the presence of an LVD lowers *substantially* the energy of vacancy formation. The question was: is this general or is it limited to the few systems that were examined? To answer this question the PI performed additional calculations¹⁻⁵. He generalized these findings to conjecture that *all LVDs make it easier to remove surface oxygen from the doped oxide than from the undoped one*. Doping with an LVD makes the doped oxide a better oxidant than the undoped oxide.

B2. LVDs make surface oxygen more reactive. It is frequently assumed that a modification that makes it easier to remove oxygen also makes that oxygen more reactive. Earlier work by the PI has shown that the presence of LVDs on an oxide surface increases the catalytic activity for CO oxidation^{14,16,17} and facilitates the dissociative adsorption of methanol¹⁹. In the period reviewed here the PI concentrated on the activation of methane by doped oxides^{1-3,6}. The rate-limiting step in the activation of methane is the breaking of the C-H bond. The PI has shown that the activation energy for the breaking of the C-H bond in methane is much lower on an oxide doped with an LVD (e.g. Zn-doped La_2O_3) than on the host oxide (La_2O_3). Experiments with Pt-doped ceria found that this material performs partial oxidation of methane with oxygen or CO_2 at

temperatures at which undoped ceria is inactive, confirming thus qualitatively the predictions of the calculations⁶.

B3. LVDs located in the bulk can activate surface oxygen. When doped oxides are prepared, one cannot control the position of the dopant in the grains of the catalyst powder; the dopant may be in the surface layer or in the bulk, or both. A chemist would naturally assume that a dopant affects only the oxygen atoms in its vicinity, by disrupting locally the chemical bonds. This has been confirmed by all calculations. Calculations performed by the PI have shown² that LVDs affect the chemistry of oxygen atoms that are far from the dopant.

B4. Adsorbed charge donors diminish the effect of the LVDs (the chemical compensation effect). A low-valence dopant creates an “electron deficit” in the host oxide. If La(III) replaces Ce(IV) in CeO₂, fewer electrons are available for the surface oxygen atoms and they become more reactive. One would think that adsorbing electron donors on the doped surface should restore (roughly) the number of electrons and render surface oxygen less reactive. Calculations performed by the PI show that this is true for several oxide surface doped with several LVDs. For example, CeO₂ doped with La will readily adsorb methane dissociatively. However, if the doped surface has a hydrogen atom on it (as a hydroxyl), its reactivity is very close to that of the undoped surface. The presence of H (electron donor) cancels the chemical effect of the La dopant. The effect, which the PI calls ‘chemical compensation’ was demonstrated for many oxides doped with LVDs and the PI postulated that this effect is general for all oxides doped with LVDs. *Adsorbing an electron donor on the surface of an oxide doped with an LVD tends to cancel the beneficial effects of the dopant: the presence of the electron donor makes the doped oxide practically as inactive as the undoped oxide.* Hydroxyls are present on practically all oxide surfaces and they are produced during catalytic reactions involving alkane. For this reason this rule is important for catalysis.

B5. An oxide doped with a LVD can catalyze oxidation reaction using CO₂ as an oxidant. In that case the reduced surface is the catalyst. While studying Ru-doped ceria⁷ for the oxidation of methane to syngas or for the hydrogenation of CO₂ to methane, the PI found that the catalyst is the reduced oxide surface. *The role of the LVD is to facilitate surface reduction.* The explanation for this observation is simple. Both CH₄ and H₂ are good reducing agents and they consume oxygen from the surface of the doped oxide. CO₂ is a weak oxidant and as a result, at

steady state, the catalyst surface (exposed simultaneously to the reductant and to CO₂) is depleted of oxygen: the reduced surface is the catalyst. It is not clear how general this observation is, but it opens the possibility of manipulating catalysis by adding a small amount of reductant to the gas feed to keep the surface reduced and modify its catalytic activity.

C. The common properties of high-valence dopants (HVD) in irreducible oxides

C1. High-valence dopants (HVDs) make an irreducible oxide a poorer oxidant. The PI generalized the results of numerous calculations (many unpublished) to state the following propensity rule: *HVDs strengthen the bond of the neighboring surface oxygen to the oxide. They make the doped oxide a poorer oxidant than the undoped one.* For extremely stable oxides, such as MgO, CaO, La₂O₃, this effect is small but it is rather large for less stable oxides.

C2. HVDs at the surface of an irreducible oxide adsorb O₂ and activate it. All HVDs in irreducible oxides that we have examined so far adsorb O₂ molecules from the gas phase (see Figure 1 for an example) and activate them^{15,9}. The PI observed two limiting cases. Case 1. The adsorbed oxygen molecule has a much longer bond than the gas-phase O₂ and a considerable negative charge, because the anti-bonding π^* orbital of O₂ becomes populated when the

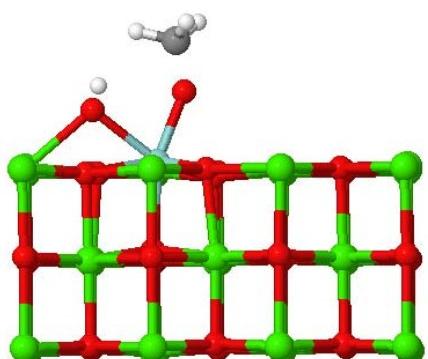


Figure 1. Methane dissociation on Zr-doped CaO. CH₄ reacts with O₂ adsorbed on the Zr dopant.

adsorption takes place. The adsorbed O₂ reacts readily⁸ with CO to make an adsorbed “carbonate”, and with methane to make OH and OCH₃, both bound to the dopant (see Figure 1). This oxidation mechanism is different from the normal Mars-van Krevelen mechanism, since the adsorbed oxygen (not the surface oxygen) is the oxidant. This prediction has been verified by experiments⁸, which measured the oxidation of C¹⁶O by ¹⁸O₂, catalyzed by ZnO doped with Ti or Al.

The experiments showed that the reaction produces C¹⁶O¹⁸O, which indicates that the added oxygen originates from the adsorbed ¹⁸O₂, not from the surface oxygen atoms (which are ¹⁶O). Recent calculations⁹ on CaO doped with La or Zr and on Nb or NiO doped with Nb have shown that these dopants adsorb O₂ and this reacts with and dissociates CH₄ with an activation energy of ~0.7 eV. Case 2. The oxygen binds so strongly to the dopant that it will not participate in catalytic chemistry. This happens for example for Nb-doped NiO. The oxygen molecule is so

strongly bound to Nb that it will not participate in catalytic chemistry. In such cases it is more appropriate to consider that the NbO₂ (the dopant with the O₂ molecule adsorbed on it) is the dopant. Calculations show that NbO₂ acts as a low-valence dopant. These examples were extrapolated to propose the following propensity rule: *all HVDs on the surface of an irreducible oxide, whose valence is higher than but close to that of the cation being replaced, adsorb O₂ from the gas phase and activate it so that it engages easily in catalytic oxidation reactions. In particular, the adsorbed O₂ reacts with methane to form adsorbed OH and OCH₃. If the valence of the dopant exceeds by much that of the cation being substituted, the O₂ binds too strongly and the dopant-O₂ complex should be considered the catalyst.* This rule needs more examples and the PI is working in this direction.

C3. High-valence dopants on the surface of reducible oxides. In a recent publication² the PI has shown that when CeO₂ is doped with Mo, W, Ta or Nb (valence VI and V, respectively), Mo and W lose two electrons which reduce two Ce⁴⁺ ions to Ce³⁺ and Ta and Nb lose one electron through a similar mechanism. Because of this, high-valence dopants in a reducible oxide are no longer high-valence; all of them have four valence electrons and their effect on the chemistry of the oxide is small.

C4. The stability of doped oxides. Preliminary work has shown that sometimes the doped oxide is not stable under reaction conditions. For example, Pd-doped ceria used for methane partial oxidation becomes quickly metallic Pd supported on ceria. The stability of the doped oxides is a subject pursued currently in the PI's group.

D. The Lewis acid-base chemistry on oxide surfaces. During the duration of this grant the PI generated a very large data base regarding the properties of oxide surfaces relevant to catalysis. In a recent article⁹ he has shown that practically all the results obtained over the years in his group and by other researchers can be understood in terms of a strong interaction between Lewis bases and Lewis acids.

E. Oxide clusters supported on oxides. Supported VO_x clusters turn out to be better oxidation catalysts²⁰⁻²² than bulk V₂O₃ or V₂O₅. The PI studied in detail^{10,11} the mechanism of CH₃OH oxidation to CH₂O by isolated VO_x clusters on TiO₂. He focused on determining the most likely stoichiometry of the cluster (i.e. x in VO_x) and calculated the reaction pathway and the activation

energy for the rate-limiting step. The reaction proceeds through the dissociation of the methanol to form a methoxide and a hydroxyl. The rate-limiting step is the removal of a H atom from the CH₃ group in the methoxide. He found two mechanisms that have about the same rate.

F. The adsorption of DNA bases on small Ag clusters. The previous grant supported work on the properties of small metal clusters. During the funding period reviewed here the PI published a paper in which he examined the photon absorption spectrum of DNA bases bound to small Ag clusters¹². The goal of the work was to help understand experimental work performed by Professor Gwinn at UCSB.

G. Kinetics in catalysis. The concept of rate-controlling step is often used in the kinetics of catalytic processes. The PI has published a paper¹³ in which he examined, by using kinetic Monte Carlo simulations, the extent to which this concept can be applied to catalysis. He has shown that, in some cases the concept is useful and in others it provides no usable information. The message is that this concept must be used with care and its predictions analyzed critically.

H. Cumulative list of people involved in the research effort. PI Horia Metiu; postdoctoral researchers Bo Li, Zhenpeng Hu, Xiaoying Sun; graduate student Jie Yu; visiting graduate student Hyun-You Kim.

I. References

II. Publications stemming from the research effort

1. B. Li and H. Metiu, Dissociation of methane on La₂O₃ surfaces doped with Cu, Mg, or Zn. *J. Phys. Chem. C* **115**, 18239-18246 (2011)
2. Z. Hu and H. Metiu, Effect of dopants on the energy of oxygen-vacancy formation at the surface of ceria: Local or global? *J. Phys. Chem. C* **115**, 17898-17909 (2011)
3. Z. Hu, B. Li, X. Sun, and H. Metiu, Chemistry of doped oxides: The activation of surface oxygen and the chemical compensation effect. *J. Phys. Chem. C* **115**, 3065-3074 (2011)
4. B. Li and H. Metiu, DFT studies of oxygen vacancies on undoped and doped La₂O₃ surfaces. *J. Phys. Chem. C* **114**, 12234-12244 (2010)
5. B. Li and H. Metiu, Does halogen adsorption activate the oxygen atom on an oxide surface? I. A study of Br₂ and HBr adsorption on La₂O₃ and La₂O₃ doped with Mg or Zr. *J. Phys. Chem. C* **116**, 4137-4148 (2012)
6. W. Tang, Z. Hu, M. Wang, G. D. Stucky, H. Metiu, and E. W. McFarland, Methane complete and partial oxidation catalyzed by Pt-doped CeO₂. *J. Catalysis* **273**, 125-137 (2010)

7. S. Sharma, Z. Hu, P. Zhang, E. W. McFarland, and H. Metiu, CO₂ methanation on Ru-doped ceria. *J. Catalysis* 278, 297-309 (2011)
8. R. G. S. Pala, W. Tang, M. M. Sushchikh, J.-N. Park, A. J. Forman, G. Wu, A. Kleiman-Shwarsctein, J. Zhang, E. W. McFarland, and H. Metiu, CO oxidation by Ti- and Al-doped ZnO: Oxygen activation by adsorption on the dopant. *J. Catalysis* 266, 50-58 (2009)
9. H. Metiu, S. Chrétien, Z. Hu, B. Li, and X. Sun, Chemistry of Lewis acid-base pairs on oxide surfaces. *J. Phys. Chem. C* (published online 30 March 2012)
10. H. Y. Kim, H. M. Lee, and H. Metiu, Oxidative dehydrogenation of methanol to formaldehyde by a vanadium oxide cluster supported on rutile TiO₂(110): Which oxygen is involved? *J. Phys. Chem. C* 114, 13736-13738 (2010)
11. H. Y. Kim, H. M. Lee, R. G. S. Pala, and H. Metiu, Oxidative dehydrogenation of methanol to formaldehyde by isolated vanadium, molybdenum, and chromium oxide clusters supported on rutile TiO₂(110). *J. Phys. Chem. C* 113, 16083-16093 (2009)
12. V. Soto Verdugo, H. Metiu, and E. Gwinn, The properties of small Ag clusters bound to DNA bases. *J. Chem. Phys.* 132, art. no. 195102 (2010)
13. H. Meskine, S. Matera, M. Scheffler, K. Reuter, and H. Metiu, Examination of the concept of degree of rate control by first-principles kinetic Monte Carlo simulations. *Surface Science* 603, 1724-1730 (2009)

I2. Prior related work from the PI's group

14. S. Chrétien and H. Metiu, Density functional study of the CO oxidation on a doped rutile TiO₂(110): Effect of ionic Au in catalysis. *Catalysis Lett.* 107, 143-147 (2006)
15. R. G. S. Pala and H. Metiu, Modification of the oxidative power of ZnO(1 0 $\bar{1}$ 0) surface by substituting some surface Zn atoms with other metals. *J. Phys. Chem. C* 111, 8617-8622 (2007)
16. V. Shapovalov and H. Metiu, Catalysis by doped oxides: CO oxidation by Au_xCe_{1-x}O₂. *J. Catalysis* 245, 205-214 (2007)
17. M. Nolan, V. Soto Verdugo, and H. Metiu, Vacancy formation and CO adsorption on gold-doped ceria surfaces. *Surface Science* 602, 2734-2742 (2008)
18. H. Y. Kim, H. M. Lee, R. G. S. Pala, V. Shapovalov, and H. Metiu, CO oxidation by rutile TiO₂(110) doped with V, W, Cr, Mo, and Mn. *J. Phys. Chem. C* 112, 12398-12408 (2008)
19. R. G. S. Pala and H. Metiu, Selective promotion of different modes of methanol adsorption via the cation substitutional doping of a ZnO surface. *J. Catal.* 254, 325-331 (2008)

I3. Other work cited

20. I. E. Wachs, Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials. *Catalysis Today* 100, 79-94 (2005)
21. B. M. Weckhuysen and D. E. Keller, Chemistry, spectroscopy and the role of supported vanadium oxides in heterogeneous catalysis. *Catalysis Today* 78, 25-46 (2003)
22. H. J. Freund, Model studies in heterogeneous catalysis. *Chemistry – A European Journal* 16, 9384-9397 (2010)